# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-029730
(43)Date of publication of application : 29.01.2002

(51)Int.Cl. C01B 33/18
G03G 9/08

(21)Application number : 2000-215910
(22)Date of filing : 17.07.2000

(71)Applicant : TITAN KOGYO KK
(72)Inventor : MORISHITA MASAYASU
YOSHINAGA TOSHIHIRO
SEKI TOSHIMASA

## (54) HYDROPHOBIC FINE PARTICLES AND THEIR APPLICATION

(57)Abstract:
PROBLEM TO BE SOLVED: To relatively easily and inexpensively provide fine particles for a toner additive having high hydrophobicity and negative chargeability and excellent in fluidity and stability of the charged state against an environmental change.
SOLUTION: Fine silica particles are coated with 1-30 wt.% hydroxide or oxide of one or more among titanium, tin, zirconium and aluminum based on the amount of the particles in a water system to prepare a slurry and further coating with 3-50 wt.% alkoxysilane based on the solid content of the slurry, neutralization with an alkali, filtration, washing, drying and comminution are carried out to produce the objective hydrophobic fine particles having high hydrophobic property and negative chargeability and useful as an additive for an electrophotographic toner for forming a copied image with a copying machine, a laser printer or the like.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

Searching PAJ

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention has high hydrophobicity and negative triboelectric charging, and relates to the toner for electrophotography which has improved sharply a fluidity, the electrification stability over an environmental variation, and an image property a hydrophobic particle useful as an external additive of the toner for electrophotography for forming copy images, such as a copying machine and a laser beam printer, etc., and by containing this hydrophobic particle.
[0002]
[Description of the Prior Art] The silica powder of a particle is widely used as an external additive aiming at a fluid improvement or electrification control in the toner for electrophotography for forming copy images, such as a copying machine and a laser beam printer. However, silica powder is the acid, and tended to adsorb moisture under that negative triboelectric charging is too strong and the effect of a surface water acid radical, and it had a fault, like the electrification change to an environmental variation is large. Although performing surface treatment, or adding an amino-group content organic compound for a silica powder front face further using a hydrophobing agent like a silane coupling agent like JP,6-19583,B, and reducing negative triboelectric charging is performed in order to prevent this, hydrophobing processing is imperfect, or an affinity [ as opposed to water by containing the amino group ] is discovered under strong effect, and it has come to attain enough the purpose of a fluid improvement and electrification nature control of a toner.
[0003] Moreover, although the electrification change to an environmental variation is small good since adsorbent [ of moisture ] is very low compared with a silica when the powder which performed the same hydrophobing processing as the above to particles, such as titanium oxide and an alumina, is used as a toner external additive For example, the negative triboelectric charging as matter was very small compared with the silica, and the capacity as a regulator for giving electrification was what inferior as indicated by JP,7-3601,B.
[0004]
[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned conventional trouble, and aims at offering the hydrophobic particle useful as a toner external additive for electrophotography which has high hydrophobicity and negative triboelectric charging. This invention aims at offering the toner for electrophotography which has improved sharply a fluidity, the electrification stability over an environmental variation, and an image property by containing such a hydrophobic particle again.
[0005]
[Means for Solving the Problem] As a result of repeating research wholeheartedly that the above-mentioned purpose should be attained, when this invention person etc. has the amount of frictional electrifications and specific surface area to iron powder and this hydrophobic particle uses him as a toner external additive whenever [ hydrophobing / of specification / the hydrophobic particle generated by the specific approach ], he completes a header and this invention for excelling in a fluidity and the electrification stability over an environmental variation.
[0006] this invention person etc. used for the nucleus first the titanium oxide particle which was excellent in the electrification stability over an environmental variation compared with the silica, and

performed various examination including hydrophobing processing. Consequently, it was possible by raising examination or the amount of covering of the class of hydrophobing agent to have obtained hydrophobic high powder. However, as the above-mentioned Prior art also touched, problems, such as a fluid fall of the externally adding toner by the fall of specific surface area or a negative triboelectric charging fall by the hydrophobing agent, occurred. Then, the negative triboelectric charging high silica particle was used for the nucleus as a following means, and the hydrophobing processing by the drainage system aiming at uniform surface treatment was tried. however, high target hydrophobicity [ the coverage of the hydrophobing agent at the time of using a silica particle alone is very low, therefore ] is acquired -- not having -- in addition -- and it was what the high negative triboelectric charging of silica original discovers since the covering condition of a hydrophobing agent is uneven also about negative triboelectric charging, and it is hard to use as a toner external additive. As a result of continuing examination in order to solve this problem, it resulted in the following knowledge.
(1) The silica particle was used as the nucleus in order to obtain good negative triboelectric charging.
(2) What covered the metal hydroxide or the metallic oxide beforehand to the silica particle was made into **** for the improvement in coverage of the hydrophobing agent to a silica particle.
(3) Covering of a metal hydroxide or a metallic oxide was performed by the drainage system, homogeneity and in order to make it good. In covering processing of a drainage system, the metallic compounds which can be treated as an acid or an alkali solution were used.
(4) In order to give high hydrophobicity, alkoxysilane was used as a hydrophobing agent covered to the aforementioned machine face.
That is, the coverage of the hydrophobing agent made to cover next was able to be raised by leaps and bounds by making a specific metal hydroxide or a specific oxide cover previously to a silica particle. Moreover, it was found out that become uniform also about a covering condition since coverage improved, and adjustment also of negative triboelectric charging is further attained with the hydroxide or oxide on the front face of a silica. This invention is completed based on the above-mentioned knowledge.
[0007] That is, the hydrophobic particle of this invention is characterized by having covered the hydroxide or oxide more than a kind of titanium, tin, a zirconium, and aluminum to the silica particle, and covering alkoxysilane with a drainage system to a ******** machine face.
[0008] Moreover, the hydrophobic particle of this invention is characterized by for 40 - 90% and specific surface area being [ for whenever / hydrophobing ] 40-350m2/g, and the amounts of frictional electrifications to iron powder being -50 - -500microC/g.
[0009] Moreover, the sum of the amount of covering of the hydroxide more than a kind of the titanium covered by said silica particle, tin, a zirconium, and aluminum or an oxide can be made into 1 - 30 % of the weight to said silica particle.
[0010] Moreover, said alkoxysilane is expressed with general formula RnSiR'm (R: a hydrocarbon group, a glycidoxy radical, an methacrylic radical or a sulfhydryl group, an R':alkoxy group, the integer of n=1-3, the integer of m=1-3, n+m=4), and the amount of covering can be made into 3 - 50 % of the weight to the aforementioned machine face.
[0011] Furthermore, the toner for electrophotography can be manufactured, using said hydrophobic particle as an external additive.
[0012]
[Embodiment of the Invention] the specific surface area of a silica particle used as the nucleus of the hydrophobic particle of this invention -- 50-400m2/g -- it is 70-380m2/g preferably. Since the particle size which carries out behavior becomes large and it becomes impossible to play sufficient role in the field of fluid grant when it is used as a toner external additive, the case of under 50m2/g is not desirable. Moreover, if 400m2/g is exceeded, since the particle size which carries out behavior on a toner front face becomes small too much, the particle on the front face of a toner is gradually buried by friction with the carrier by churning, or friction with a blade or a sleeve and a fluidity and electrification nature change, it is not desirable.
[0013] Moreover, it is desirable still more desirable that they are -50 - -500microC/g, and the amounts [ as opposed to / whenever / hydrophobing / is / 40 - 90% and the specific surface area of the hydrophobic particle of this invention / 40-350m2/g, and / iron powder ] of frictional electrifications are -50 - -400microC/g. However, the water solution containing the methanol of predetermined

concentration is prepared by unit 2.5% of the weight, and "whenever [ hydrophobing ]" carries out little addition of the powder to measure at the liquid, and judges it by sedimentation initiation by viewing. The display is the methanol concentration of sedimentation initiation.

[0014] Whenever [ said hydrophobing ] is 60 - 90% especially preferably 50 to 90% still more preferably. When externally adding is carried out to a toner less than 40% of case, the electrification change under [ originating in adsorption moisture ] highly humid is not greatly desirable. moreover -- in exceeding 90%, while it is necessary to make the addition or carbon number of a processing agent increase and condensation becomes strong by debt of a chain -- the fall of specific surface area -- happening -- in addition -- and it is not desirable in order that the negative triboelectric charging of a silica particle used as a nucleus may decrease.

[0015] Moreover, it is important that the specific surface area after hydrophobing processing is also 40-350m2/g. That is, the case of under 40m2/g, since the particle size which carries out behavior becomes large and it becomes impossible to play sufficient role in fields, such as fluid grant, when it is used as a toner external additive, it is not desirable. Moreover, if 350m2/g is exceeded, since the particle size which carries out behavior on the toner front face which carried out externally adding becomes small too much, the particle on the front face of a toner is gradually buried by friction with the carrier by churning, or friction with a blade or a sleeve and a fluidity and electrification nature change, it is not desirable.

[0016] Furthermore, it is important that negative triboelectric charging is also high. For example, although the electrification change to a fluidity or an environmental variation etc. is small good when the powder which performed hydrophobing processing to particles, such as titanium oxide and an alumina, is used as a toner external additive Although adding the matter with still stronger negative triboelectric charging, such as a silica, is generally performed in order that the negative triboelectric charging as matter may compensate it, since it is very low compared with a silica, there is a bad influence that the electrification change to an environmental variation becomes large, by adding a silica. Moreover, as a recent trend, electrophotography copy images, such as a copying machine and a printer, have shifted to FURUKARA from monochrome, and in order to satisfy the image property of the color tone repeatability and transparency which are demanded in this case, generally toner resin has shifted to negative triboelectric charging polyester system resin. For this reason, it has become important that the powder used as an external additive also has high negative triboelectric charging, and the hydrophobic particle of this invention whose amount of frictional electrifications to iron powder is -50--500microC/g is suitable.

[0017] Moreover, as for the hydrophobic particle of this invention, it is desirable that the sum of the amount of covering of the hydroxide more than a kind of the titanium covered by said silica particle, tin, a zirconium, and aluminum or an oxide is 1 - 30 % of the weight to said silica particle, and it is still more desirable that it is 3 - 25 % of the weight. Since the effectiveness which controls the negative triboelectric charging of a silica particle not being acquired, and the coverage of a hydrophobing agent which processes succeedingly do not improve in less than 1% of the weight of a case, it is not desirable. Moreover, when exceeding 30 % of the weight, since condensation of silica particles occurs and specific surface area falls, it is not desirable.

[0018] Moreover, the aforementioned alkoxysilane is expressed with general formula RnSiR'm (R: a hydrocarbon group, a glycidoxy radical, an methacrylic radical or a sulfhydryl group, an R':alkoxy group, the integer of n=1-3, the integer of m=1-3, n+m=4), and, as for the hydrophobic particle of this invention, it is desirable that the amount of covering is 3 - 50 % of the weight to the aforementioned machine face.

[0019] As alkoxysilane, it is general formula RnSiR'mR. : Alkyl group, Hydrocarbon groups, such as alkenyl radicals, such as aryl groups, such as a phenyl group, and a vinyl group, an alkynyl group, a cycloalkyl radical, or a cyclo alkenyl radical, Or glycidoxy radical, methacrylic radical, or sulfhydryl group n : Integer R' of 1-3: Alkoxy group m : It is what is expressed with integer n+m=4 of 1-3. For example, vinyltrimetoxysilane, methyl trimetoxysilane, propyltrimethoxysilane, i-butyltrimethoxysilane, n-butyltrimethoxysilane, n-hexyl trimethoxysilane, n-octyl trimethoxysilane, n-decyltrimetoxysilane, phenyltrimethoxysilane, 3-glycidoxypropyltrimetoxysilane, etc. can be mentioned, and the thing of 1-10 has the desirable carbon number of a hydrocarbon group R. although, as for 11 or more things, a carbon number becomes high whenever [ hydrophobing ], while chain length is too long, a chain is involved and condensation becomes strong -- the fall of specific surface area -- happening -- in addition -- and it

is not desirable in order that the negative triboelectric charging of a silica particle used as a nucleus may decrease. Moreover, although the emulsion of silicone oil, such as poly dimethylsiloxane, and the coupling agent of a titanate system are also effective in order to raise whenever [ hydrophobing ], it is not desirable from the same reason. In addition, alkoxysilane can also use together and use two or more sorts.

[0020] The amount of covering of alkoxysilane is 3 - 50 % of the weight to the aforementioned machine face, and is 3 - 40 % of the weight preferably. To less than 3% of the weight of a case, since whenever [ hydrophobing ] becomes low, it is not desirable. Moreover, when exceeding 50 % of the weight, since specific surface area falls and particle size becomes large, it is not desirable.

[0021] The manufacture approach of the hydrophobic particle in this invention typically The silica particle which has the specific surface area of 50-400m2/g by the drainage system Titanium, Said silica particle is received in the hydroxide or oxide more than a kind of tin, a zirconium, and aluminum. After considering as the slurry covered one to 30% of the weight and covering alkoxysilane three to 50% of the weight to the solid content in said slurry succeedingly, alkali neutralizes and it is characterized by performing filtration, washing, desiccation, and grinding.

[0022] As long as the silica particle used as a nucleus has the specific surface area of 50-400m2/g, it may use the particle of the gap manufactured by the wet method or the gaseous-phase method.

[0023] The slurry temperature at the time of covering the hydroxide or oxide more than a kind of titanium, tin, a zirconium, and aluminum with a drainage system performs said silica particle at 20-90 degrees C. By making slurry temperature into said value, covering of the inorganic metal hydrate on the front face of a silica becomes good, and the coverage of the hydrophobing agent covered succeedingly improves.

[0024] Moreover, if it is the matter which can be dealt with as an acid or an alkali solution as the titanium covered with a drainage system to a silica particle, tin, a zirconium, and a source of aluminum, what kind of thing may be used, for example, chlorination tin, stannous sulfate, etc. can use an aluminum sulfate, a sodium aluminate, etc. together for sulfuric-acid titanium, a titanium tetrachloride, etc. in the combination of independent or arbitration as a source of a zirconium as a tin source as a source of titanium as a source of aluminum, such as zirconium oxychloride, a sulfuric-acid zirconium and a zirconium nitrate,.

[0025] Furthermore, in case alkoxysilane is covered succeedingly, 2-6, and after adjusting to pH 3-6 preferably, specified quantity addition of the alkoxysilane is carried out for pH of a slurry, 20-100 degrees C of temperature of a slurry are preferably adjusted to 30-70 degrees C, and hydrolysis and a condensation reaction are performed. Alkoxysilane uses two or more sorts together, using the aforementioned thing independently.

[0026] moreover, the purpose which promotes a condensation reaction after carrying out churning maintenance of said slurry -- alkali -- using -- pH 4-9 -- it neutralizes so that it may be preferably set to 5-7. As alkali used for neutralization, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, aqueous ammonia, ammonia gas, etc. can be used, for example. Thus, by processing, the hydrophobic particle without re-condensation with which the hydrophobing agent was covered by homogeneity is obtained.

[0027] 100-190 degrees C of drying temperature after filtration and rinsing are 110-170 degrees C preferably. Since whenever [ hydrophobing ] will worsen [ drying efficiency ] low if it is less than 100 degrees C, it is not desirable. Moreover, if it exceeds 190 degrees C, since the fall of whenever [ discoloration and hydrophobing ] will take place by the pyrolysis of a hydrocarbon group, it is not desirable.

[0028] As another gestalt of the manufacture approach of the hydrophobic particle in this invention, the silica particle which has the specific surface area of 50-400m2/g is made into the slurry which covered the hydroxide or oxide more than a kind of titanium, tin, a zirconium, and aluminum with the drainage system one to 30% of the weight to said silica particle, and filtration, washing and desiccation, and after [ if, ] calcinating further, said alkoxysilane can also be covered with dry type for this using a Henschel mixer etc.

[0029] Although the processing object which desiccation ended is soft since the hydrophobing agent is covered good, and you may use it as a toner external additive as it is, the dispersibility on the front face of a toner improves sharply by grinding with pulverizers, such as a hammer mill and a fluid energy mill,

further.
[0030] Moreover, externally adding of the hydrophobic particle of this invention can be carried out, and the toner for electrophotography can also be manufactured. As a toner, it can be used for any toners for electrophotography, such as magnetic one component, nonmagnetic 1 component, and two components, and a well-known thing can be used for arbitration about the constituent of a toner.
[0031] That the addition to the toner of the hydrophobic particle of this invention should just be an amount which serves as a property for which the toner obtained asks, although especially a limit is not carried out, considering as 0.1 - 4 % of the weight preferably can usually add to a toner by the desirable and well-known approach 0.05 to 5% of the weight. The improvement of the fluidity of a toner or electrification nature is not accepted in less than 0.05% of the weight of a case, and it is not desirable to it. Moreover, when exceeding 5 % of the weight, it is not desirable in order for the hydrophobic particle of this invention to secede from a toner front face, to become the cause of contamination of a photo conductor or a carrier since the particle which carries out behavior independently increases, and to have a bad influence on an image property.
[0032] Moreover, in case a toner is manufactured, the hydrophobic particle of this invention is not restricted, but can combine two or more kinds of hydrophobic particles which belong to this invention if needed, or can also use together other additives, such as fixing assistants, such as lubricant, such as oxide particles, such as titanium oxide and an alumina, and Teflon (trademark), zinc stearate, polyvinylidene fluoride, or polyethylene, and polypropylene, with what is used independently.
[0033]
[Example] Although an example and the example of a comparison are given to below and this invention is further explained to a detail, these are not described only for instantiation and the range of this invention is not restricted by these.
[0034]
[Example 1] 100g (specific-surface-area 130m2/[ of Acrosil #130 and a base silica ] g, product made from Japanese Aerosil) of gaseous-phase method silica particles was distributed in the water of 2L, solution temperature was warmed at 70 degrees C, and as TiO2, sulfuric-acid titanium solution 30mL and 5-N sodium-hydroxide water solution of 100 g/L were dropped at coincidence so that pH might be set to 6.0 (it is also only hereafter called "inorganic processing"). After cooling solution temperature to 40 degrees C after dropping termination and adjusting pH to 4.0, n-hexyl trimethoxysilane 25g was added succeedingly. After 4-hour churning maintenance, 2-N sodium-hydroxide water solution was added, pH was adjusted to 6.5, and filtration and rinsing were performed after carrying out churning maintenance for further 2 hours. After drying at 130 degrees C, the cake rinsed [ filtration and ] was pulverized with the pulverizer by the air-jet method, and obtained the hydrophobic particle made into the purpose.
[0035]
[Example 2] In the example 1, the addition of a sulfuric-acid titanium solution was set to 100mL(s), and also it processed similarly, and the hydrophobic particle made into the purpose was obtained.
[0036]
[Example 3] In the example 1, the addition of a sulfuric-acid titanium solution was set to 250mL(s), and also it processed similarly, and the hydrophobic particle made into the purpose was obtained.
[0037]
[Example 4] In the example 2, the gaseous-phase method silica particle was set to Aerosil #200 (specific-surface-area 200m2/g of a base silica, product made from Japanese Aerosil), and also it processed similarly, and the hydrophobic particle made into the purpose was obtained.
[0038]
[Example 5] 100g (specific-surface-area 380m2/[ of Aerosil #380 and a base silica ] g, product made from Japanese Aerosil) of gaseous-phase method silica particles was distributed in the water of 4L, solution temperature was warmed at 70 degrees C, and as TiO2, sulfuric-acid titanium solution 200mL and 5-N sodium-hydroxide water solution of 100 g/L were dropped at coincidence so that pH might be set to 6.0. After cooling solution temperature to 40 degrees C after dropping termination and adjusting pH to 4.0, n-hexyl trimethoxysilane 40g was added succeedingly. After 4-hour churning maintenance, 2-N sodium-hydroxide water solution was added, pH was adjusted to 6.5, and filtration and rinsing were performed after carrying out churning maintenance for further 2 hours. After drying at 130 degrees C,

the cake rinsed [ filtration and ] was pulverized with the pulverizer by the air-jet method, and obtained the hydrophobic particle made into the purpose.

[0039]

[Example 6] In the example 1, stannic chloride solution 100mL of 100 g/L was dropped as SnO2 instead of the sulfuric-acid titanium solution, and also it processed like the example 1, and the hydrophobic particle made into the purpose was obtained.

[0040]

[Example 7] In the example 1, zirconium oxychloride solution 100mL of 100 g/L was dropped as ZrO2 instead of the sulfuric-acid titanium solution, and also it processed like the example 1, and the hydrophobic particle made into the purpose was obtained.

[0041]

[Example 8] In the example 4, set the addition of a sulfuric-acid titanium solution to 300mL(s), and n-hexyl trimethoxysilane 25g was set to n-butyltrimethoxysilane 30g, and also it processed similarly, and the hydrophobic particle made into the purpose was obtained.

[0042]

[Example 9] In the example 4, set n-hexyl trimethoxysilane 25g to n-decyltrimetoxysilane 15g, and drying temperature was made into 120 degrees C, and also it processed similarly, and the hydrophobic particle made into the purpose was obtained.

[0043]

[Example 10] In the example 3, set n-hexyl trimethoxysilane 25g to n-decyltrimetoxysilane 5g, and drying temperature was made into 120 degrees C, and also it processed similarly, and the hydrophobic particle made into the purpose was obtained.

[0044]

[Example 11] 100g (specific-surface-area 50m2/g of Aerosil OX50 and a base silica, product made from Japanese Aerosil) of gaseous-phase method silica particles was distributed in the water of 2L, solution temperature was warmed at 70 degrees C, and as SnO2, stannic chloride solution 30mL and 5-N sodium-hydroxide water solution of 100 g/L were dropped at coincidence so that pH might be set to 6.0. After cooling solution temperature to 40 degrees C after dropping termination and adjusting pH to 4.0, n-hexyl trimethoxysilane 10g was added succeedingly. After 4-hour churning maintenance, 2-N sodium-hydroxide water solution was added, pH was adjusted to 6.5, and filtration and rinsing were performed after carrying out churning maintenance for further 2 hours. After drying at 130 degrees C, the cake rinsed [ filtration and ] was pulverized with the pulverizer by the air-jet method, and obtained the hydrophobic particle made into the purpose.

[0045]

[Example 12] 100g (specific-surface-area 200m2/[ of Aerosil #200 and a base silica ] g, product made from Japanese Aerosil) of gaseous-phase method silica particles was distributed in the water of 2L, solution temperature was warmed at 70 degrees C, and as aluminum 2O3, sodium-aluminate solution 50mL and 5-N sodium-hydroxide water solution of 100 g/L were dropped at coincidence so that pH might be set to 6.0. After cooling solution temperature to 40 degrees C after dropping termination and adjusting pH to 5.0, n-hexyl trimethoxysilane 20g was added succeedingly. After 4-hour churning maintenance, 2-N sodium-hydroxide water solution was added, pH was adjusted to 6.5, and filtration and rinsing were performed after carrying out churning maintenance for further 2 hours. After drying at 130 degrees C, the cake rinsed [ filtration and ] was pulverized with the pulverizer by the air-jet method, and obtained the hydrophobic particle made into the purpose.

[0046]

[The example 1 of a comparison] In the example 1, a sulfuric-acid titanium solution and n-hexyl trimethoxysilane were not added, and also it processed similarly, and the particle was obtained.

[0047]

[The example 2 of a comparison] In the example 1, a sulfuric-acid titanium solution was not added, and also it processed similarly, and the hydrophobic particle was obtained.

[0048]

[The example 3 of a comparison] In the example 2, n-hexyl trimethoxysilane was not added, and also it processed similarly, and the particle was obtained.

[0049]

[The example 4 of a comparison] The gaseous-phase method silica particle (R-972, product made from Japanese Aerosil) of inorganic processing nothing and dimethyldichlorosilane processing was used as the comparison matter of the hydrophobic particle of this invention.
[0050] As mentioned above, the measurement result of the sample of examples 1-12 and the examples 1-4 of a comparison is shown in Table 1. In this table, it writes a "base silica", and the specimen at the time of acquisition is already covering ending about dimethyldichlorosilane, and the notation "-" of the example 4 of a comparison shows that the specific surface area and its amount of covering of a base silica were not able to be measured. [ the silica particle used as the nucleus of a hydrophobic particle ] In addition, many properties of Table 1 were measured in the following ways.
[0051] Whenever [ [whenever / hydrophobing /] ] The water solution containing the methanol of predetermined concentration is prepared by unit 2.5% of the weight, and little addition of the powder to measure is carried out at the liquid, and it judges by sedimentation initiation by viewing. The methanol concentration of sedimentation initiation was displayed as wheaever [ hydrophobing ].
[0052] It measured in law one BET using the Gemini by [specific-surface-area] microphone ROMERI tex company 2375 mold specific-surface-area measuring device.
[0053] It extracted so that it might become a wide mouthed bottle with the screw made from the [amount of frictional electrifications] hard polyethylene (capacity 100mL) with 99.5:0.5 by the weight ratio about an iron powder carrier (TEFV 200/300, Powdertech make) and this hydrophobic particle, and the amount of electrifications was measured after the shaking using the amount measuring device of blowing off electrifications (TB-200 mold, Toshiba Chemical CORP. make) for 5 minutes with the arm swing mold shaking mixer.
[0054] After mixing [manufacture of toner] polyester resin, carbon black, an offset inhibitor, and an electrification regulator with a blender, melting kneading was carried out by the KRC kneader (Kurimoto make). After cooling the obtained kneading object and carrying out coarse grinding in a coarse crusher, it pulverized with the pulverizer by the air-jet method, it classified with the pneumatic elutriation machine further, and coloring resin fine particles were obtained. 1.0 section externally adding of the sample obtained in examples 1-12 and the examples 1-4 of a comparison was carried out to this fine-particles 100 section, and the black toner with a mean particle diameter of 8 micrometers was manufactured.
[0055] The bulk density (g/mL) of each toner was measured according to [fluid evaluation approach] JIS K-5101. [ 18] "bulk" measuring method. The result was written together to Table 1. In addition, a fluidity is so good that bulk density is high.
[0056] It extracted so that it might become a wide mouthed bottle with the screw made from the [electrification stability evaluation approach] hard polyethylene (capacity 100mL) with 96:4 by the weight ratio about an iron powder carrier (TEFV 200/300, Powdertech make) and a toner, and it was left for 24 hours, opening under a low-humidity/temperature environment and high-humidity/temperature (LL, 15 degrees C / 20%RH) (HH, 35 degrees C / 90%RH). The wide mouthed bottle which carried out neglect termination was sealed, and the amount of toner electrifications under each environment was measured after the shaking using the amount measuring device of blowing off electrifications (TB-200 mold, Toshiba Chemical CORP. make) for 2 minutes with the arm swing mold shaking mixer. The result was written together to Table 1. In addition, electrification stability is so good that the difference of the amount of electrifications in the environment of LL and HH is small.
[0057]
[Table 1]

| | 基体コア | | 無機処理 | | 疎水化処理 | | 粉体特性 | | | トナー特性 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 比表面積 (m²/g) | 処理酸化物 | 添加量 (wt%) | 種類 | 添加量 (g) | 疎水化度 (%) | 比表面積 (m²/g) | 真比帯電量 (μC/g) | かさ密度 (g/mL) | LL帯電量 (μC/g) | HH帯電量 (μC/g) | 帯電差Δ (μC/g) |
| 実施例1 | 130 | $TiO_2$ | 3 | n-ヘキシルトリメトキシシラン | 25 | 60.0 | 111 | -214 | 0.365 | -25 | -21 | 4 |
| 実施例2 | 130 | $TiO_2$ | 10 | n-ヘキシルトリメトキシシラン | 25 | 62.5 | 101 | -191 | 0.363 | -24 | -21 | 3 |
| 実施例3 | 130 | $TiO_2$ | 25 | n-ヘキシルトリメトキシシラン | 25 | 62.5 | 85 | -150 | 0.357 | -22 | -20 | 2 |
| 実施例4 | 200 | $TiO_2$ | 10 | n-ヘキシルトリメトキシシラン | 15 | 57.5 | 178 | -307 | 0.373 | -24 | -21 | 3 |
| 実施例5 | 130 | $TiO_2$ | 20 | n-ヘキシルトリメトキシシラン | 40 | 62.5 | 306 | -540 | 0.381 | -28 | -23 | 5 |
| 実施例6 | 130 | $SnO_2$ | 10 | n-ヘキシルトリメトキシシラン | 15 | 65.0 | 163 | -232 | 0.365 | -23 | -20 | 3 |
| 実施例7 | 130 | $ZrO_2$ | 10 | n-ヘキシルトリメトキシシラン | 25 | 62.5 | 102 | -135 | 0.361 | -23 | -21 | 2 |
| 実施例8 | 200 | $TiO_2$ | 30 | n-デシルトリメトキシシラン | 30 | 60.0 | 162 | -188 | 0.374 | -25 | -23 | 3 |
| 実施例9 | 200 | $TiO_2$ | 10 | n-デシルトリメトキシシラン | 15 | 67.5 | 155 | -169 | 0.355 | -22 | -20 | 2 |
| 実施例10 | 130 | $TiO_2$ | 25 | n-ブチルトリメトキシシラン | 5 | 55.0 | 91 | -125 | 0.360 | -24 | -20 | 4 |
| 実施例11 | 50 | $SnO_2$ | 3 | n-ヘキシルトリメトキシシラン | 10 | 65.0 | 42 | -74 | 0.336 | -19 | -17 | 2 |
| 実施例11 | 200 | $Al_2O_3$ | 5 | n-ヘキシルトリメトキシシラン | 10 | 55.0 | 184 | -418 | 0.369 | -22 | -19 | 3 |
| 比較例1 | 130 | なし | 0 | なし | 0 | 0 | 118 | -661 | 0.289 | -32 | -19 | 13 |
| 比較例2 | 130 | なし | 0 | なし | 25 | 22.5 | 113 | -275 | 0.284 | -35 | -25 | 10 |
| 比較例3 | 130 | $TiO_2$ | 10 | なし | 0 | 0 | 109 | -303 | 0.244 | -26 | -15 | 11 |
| 比較例4 | — | なし | 0 | — | — | 42.5 | 100 | -250 | 0.318 | -30 | -21 | 9 |

[0058] The following evaluation was mainly able to be obtained from the result of Table 1.
(1) By the comparison with the example 2 of a comparison which has not carried out inorganic processing, in the examples 1-12, coverage has been improved by inorganic processing so that clearly, and whenever [ hydrophobing / with any high fine particles ] was obtained.
(2) The fine particles which can give the good amount of frictional electrifications were obtained, without a silica particle reducing greatly the high negative triboelectric charging which it originally has, though it was high hydrophobicity such.
(3) In the toner property, in each example of an experiment, all had high bulk density before and after delta0.1 g/mL, and the fluidity has improved certainly rather than the example of a comparison.
(4) And each difference of the amount of electrifications of LL and HH was smaller than the example of a comparison, and the toner which was extremely excellent in electrification stability was obtained.

[Translation done.]

* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]
[Claim 1] The hydrophobic particle characterized by having covered the hydroxide or oxide more than a kind of titanium, tin, a zirconium, and aluminum to the silica particle, and covering alkoxysilane with a drainage system to a ******** machine face.
[Claim 2] The hydrophobic particle according to claim 1 characterized by for whenever [ hydrophobing ] being 40 - 90%, and for specific surface area being 40-350m2/g, and the amounts of frictional electrifications to iron powder being -50 - -500microC/g.
[Claim 3] The hydrophobic particle according to claim 1 or 2 to which the sum of the amount of covering of the hydroxide more than a kind of the titanium covered by said silica particle, tin, a zirconium, and aluminum or an oxide is characterized by being 1 - 30 % of the weight to said silica particle.
[Claim 4] The hydrophobic particle according to claim 1 to 3 to which said alkoxysilane is expressed with general formula RnSiR'm (R: a hydrocarbon group, a glycidoxy radical, an methacrylic radical or a sulfhydryl group, an R':alkoxy group, the integer of n=1-3, the integer of m=1-3, n+m=4), and the amount of covering is characterized by being 3 - 50 % of the weight to the aforementioned machine face.
[Claim 5] The toner for electrophotography using the hydrophobic particle according to claim 1 to 4 as an external additive.

---

[Translation done.]